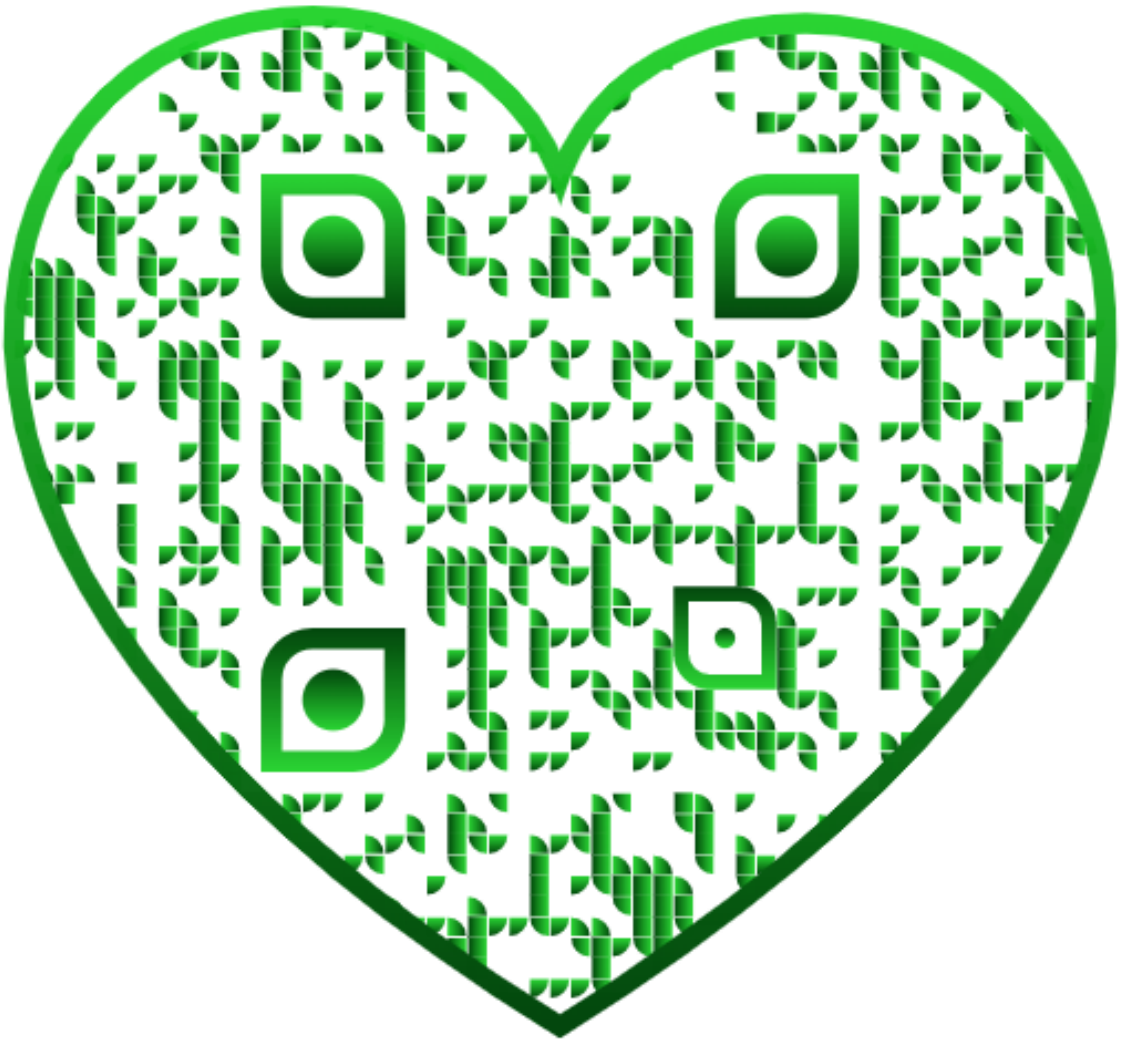
Electroanalytical Methods



Objectives

- At the end of this lesson you will able to
  - Describe electrochemical cells
  - Identify the different types of electrodes
  - Discuss the use of each type of electrodes
  - **Determine the concentration (amount) of ionic species using Nernst equation**

Brainstorming exercise

- **What do we mean by**
  - **Electricity,**
  - **Chemistry and**
  - **Electrochemistry?**
- **What is electroanalytical method?**

Introduction

- **Electrochemical method**

➢ can be defined as one in which the **electrical response** of a chemical system or sample is measured

- **The experimental system**

(A) The electrolyte

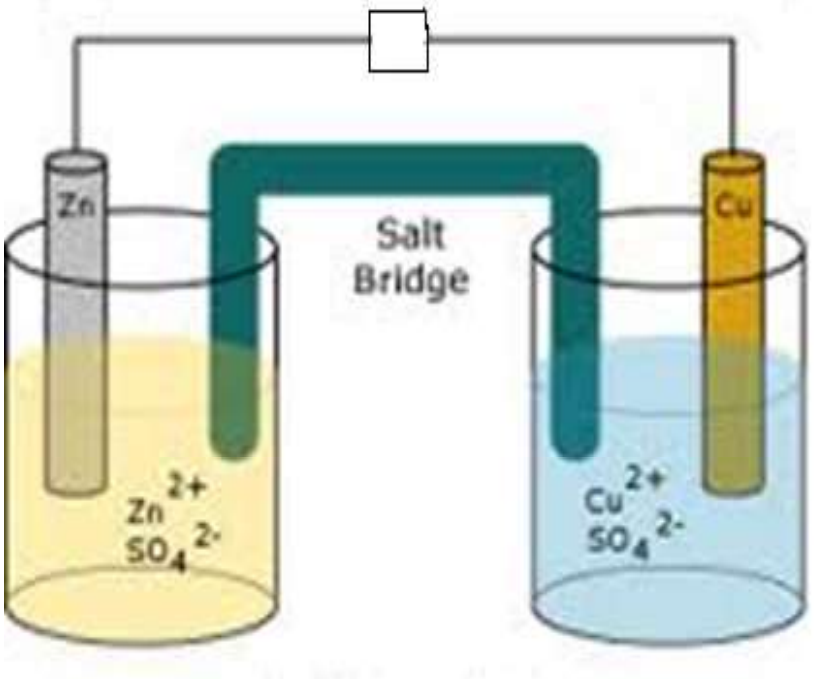
➢ a chemical system capable of conducting current

B) The measuring or external circuit,

- used to apply and to measure electrical signals

C) The electrodes,

- conductors that serve as contacts between the measuring system and electrolyte

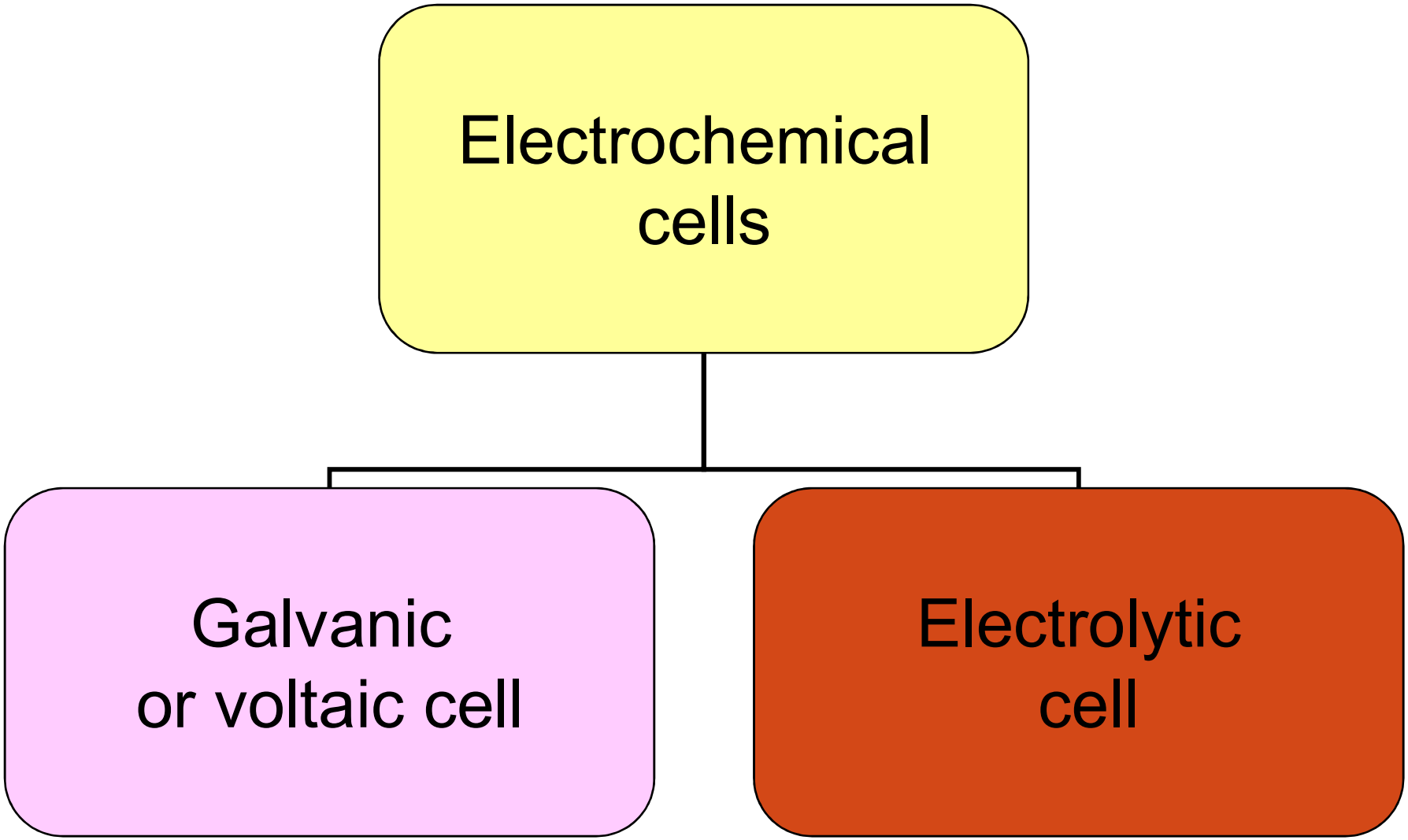


- Anodes $Zn^{2+} + 2e^- \Leftrightarrow Zn(s)$ **($E° = -0.763$)**
- Cathodes $Cu^{2+} + 2e^- \Leftrightarrow Cu(s)$ **($E° = +0.337$)**

- The experimental system assembled together to form electrochemical cell
- **Electrochemical cells:**

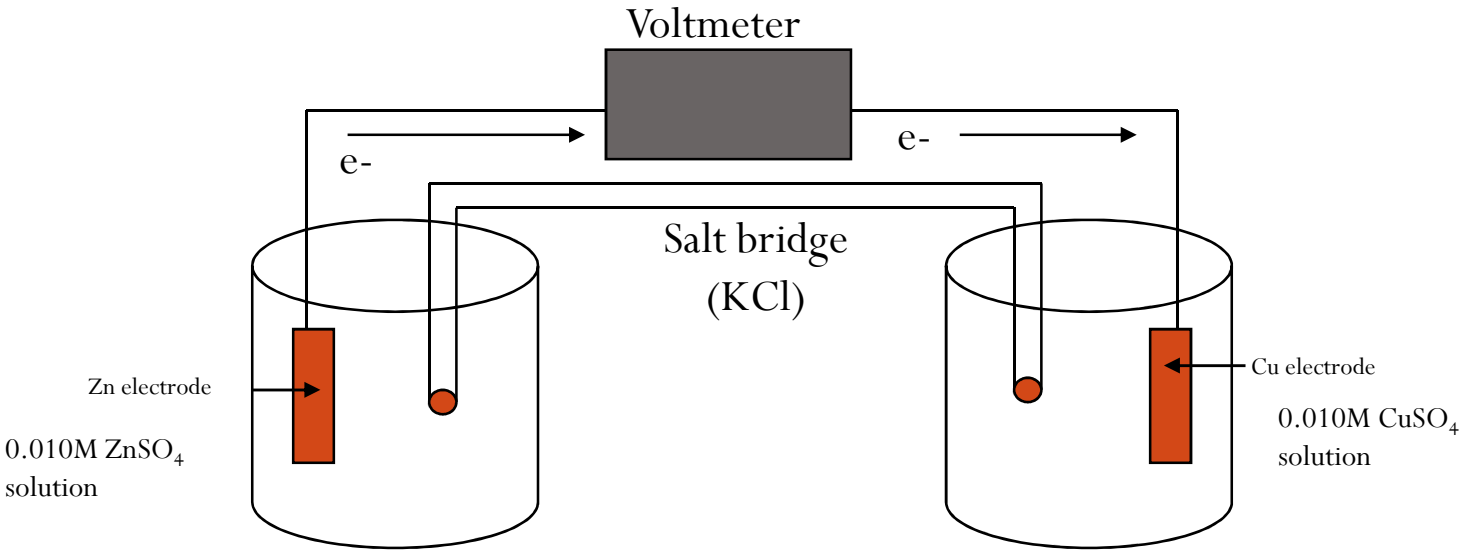
➢ are two electrodes (usually metallic) immersed in the **same electrolyte solution** or in two **different electrolyte solutions** which are in electrical contact

➢ Electrochemical cells are classed into two groups.


Electrochemical cells
Galvanic or voltaic cell
Electrolytic cell

1. Galvanic or Voltaic cells:

- electrochemical reactions occur **spontaneously,**
- Used to convert the **chemical energy** into **electrical energy**
- e.g. Zinc (Zn) wants to ionize more than copper (Cu).



$Zn \leftrightarrow Zn^{2+}(aq) + 2e^-$

$a_{Zn^{2+}} = 0.010$

Anode

$Cu^{2+}(aq) + 2e^- \leftrightarrow Cu(s)$

$a_{Cu^{2+}} = 0.010$

Cathode

- The two reactions are typically written
  - $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
  - $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

➢ Each reaction represents a half-cell reaction.

- Schematic representation of the above cell is as follows:

$Zn / Zn^{2+} (C_{zn2+}) // Cu^{2+} (C_{Cu2+}) / Cu$

The anode The cathode

- **Rules which are followed in the representation of cells are:**
  - Conventional chemical symbols are used to designate different chemical species such as ions, atoms or molecules
  - Partial pressures of gases and ionic concentrations are written in parentheses following the respective symbols
  - Two ions placed in the same solution are separated by a comma
  - A single vertical line (/) represents a metal electrolyte boundary at which a potential difference is taken into account
  - A double vertical line (//) denotes a salt bridge or equivalent device (junction potential at this location is minimized and may be ignored in calculations)

2. Electrolytic cells:

- In which **chemical reactions** are caused to occur by the imposition of an **external voltage** greater than the reversible (galvanic) voltage of the cell
- Under these circumstances, the reactions occurring at the electrodes for the above example

$$Zn^{2+} + 2e \rightleftharpoons Zn(s)$$

$$Cu(s) \rightleftharpoons Cu^{2+} + 2e$$

- Used to **carry out chemical reactions** at the **expense of electrical energy**

- In general, an electrochemical cell is a device capable of either deriving electrical energy from chemical reaction, or facilitating chemical reactions through the introduction of electrical energy

Electrode Potentials

- The reactions in an electrochemical cell can be thought of as two half-cell reactions, each with its own characteristic electrode potential
  - These measure the driving force for the reaction
  - By convention, always written as reductions

- **Standard electrode potential (E^0):** the measure of **individual potential of an electrode** at standard ambient conditions (298K, solutes at a concentration of 1 M, and gas pressure at 1 bar)

Some Standard Electrode Potentials

Reaction	E^0 at 298K (Volts)
$Cl_2(g) + 2e^- \Leftrightarrow 2\ Cl^-$	+1.359
$O_2\ (g) + 4H^+ + 4e^- \Leftrightarrow 2\ H_2O$	+1.229
$Ag^+ + e^- \Leftrightarrow Ag(s)$	+0.799
$Cu^{2+} + 2e^- \Leftrightarrow Cu(s)$	+0.337
$Hg_2Cl_2 + 2e^- \Leftrightarrow 2Hg(l) + 2\ Cl_2$	+0.268
$2H^+ + 2e^- \Leftrightarrow H_2\ (g)$	0.000
$AgI(s) + e^- \Leftrightarrow Ag(s) + I_2$	-0.151
$Cd^{2+} + 2e^- \Leftrightarrow Cd(s)$	-0.403
$Zn^{2+} + 2e^- \Leftrightarrow Zn(s)$	-0.763

Cell potential

- Energy is required to force the electrons to move from anode to the cathode electrode.
  - the amount of energy per unit charge available from the **voltaic cell** is called the electromotive force (emf) of the cell.
- Energy per unit charge is expressed in volts (1 volt = 1 joule/coulomb)
- The **emf** of a cell is the algebraic sum of the **potentials developed** across the **two electrode-solution interfaces** and the **liquid junction potential**

- For the above example:(for Zn-Cu galvanic cell)

$$E_{cell} = E_{Cu2+,Cu} + E_{lj} - E_{Zn2+,Zn}$$

Or generally :

$$E_{cell} = E_{cathode} + E_{lj} - E_{anode}$$

$E_{cell} = E_{cathode} - E_{anode}$ **for minimal** E_{lj}

The Nernst equation

- Relates the **cell potential with concentration of the analytes** involved in the electroanalytical cell

- The potential (emf or E) is the energy per unit charge and expressed in Volts (1 volt = 1 joule/coulomb)

- The amount of electric charge contained in a mole of electrons is called the Faraday constant (F)

- Faraday constant (F) = $N_a e^-$ = 6.022 x 10^{23} x 1.60221 x 10^{-19} = 96,485 Coulombs/mole
- The energy yield from a voltaic cell is given by the cell voltage times the number of moles of electrons transferred times the Faraday constant.
  - **Electrical energy output = nFE_{cell}**

- **In general:**

$\Delta G = \Delta G^\circ + RT\ln(Q)$

where R = Molar gas constant (8.314 joule/k-mole)
T = absolute temperature (K)
ΔG= change in Geb's free energy
Q= the activity of reacting species = [reduced]/[oxidized]

- However:

$\Delta G = -nFE_{cell}$

$-nFE_{cell} = -nFE^\circ_{cell} + RT\ln(Q)$

$E_{cell} = E^\circ_{cell} - (RT/nF)\ln(Q)$

$E_{cell} = E^\circ_{cell} - (0.0591/n)\log(Q)$ --------at 25 ^{0}C (298k)

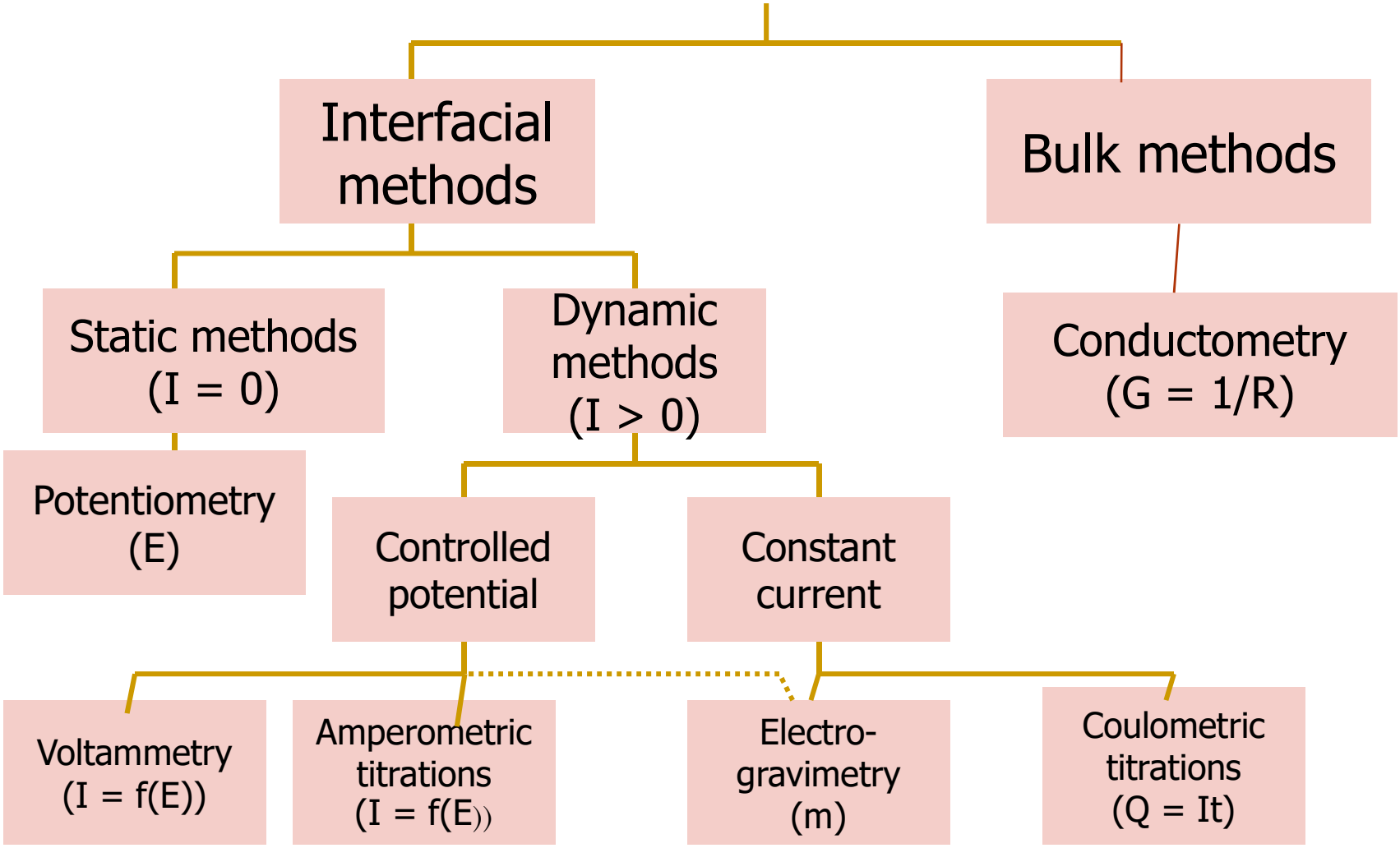
$E_{cell} = E^o_{cell} - (0.0591/n)\log[C_{product}]/[C_{reactant}]$

→ The Nernst Equation

Example practice:

- Based on the given information below, calculate the concentration of Ag^{+} (x) in a given solution
- $Pt^{o}/Fe^{2+}(0.05M),Fe^{3+}(0.25M)//Ag^{+}(xM)/Ag^{o}$
- Ecell = -0.106volt
- $Fe^{3+} + e^{-} \leftrightarrow Fe^{2+}$ $E^{o} = 0.771$volt
- $Ag^{+} + e^{-} \leftrightarrow Ag^{o}$ $E^{o}=0.799$ volt

Main Branches of Electroanalytical Chemistry



- ✓ Key to measured quantity: I = current, E = potential, R = resistance, G = conductance, Q = quantity of charge, t = time, vol = volume of a standard solution, m = mass of an electrodispensed species

- **Bulk Methods:** Based on phenomenon occurs in the bulk of solution
  - Measurement of properties of the whole solution
    - **Conductimetry** is an example
- **Interfacial Methods:** Signal is a function of phenomena taking place at the **electrode-solution interface**
  - pH measurement using a pH electrode

- **Static Methods:**
  - No current passes in the electrochemical cell
  - **e.g. Potentiometry**
- **Dynamic Methods:**
  - Current flows in the electrochemical cell
    - **Constant Current Methods**
      - ✓ Fixed current allows complete oxidation or reduction of the analyte. Quantity of electricity **(Coulometry)** or material deposited on electrodes **(Electrogravimetry)** are determined
    - **Controlled-Potential Methods:**
      - ✓ Constant potential is applied during analysis while measurements of other variables are carried out. Sensitive and can be carried out for small volumes.
      - ✓ For example**:Voltammetry**: Potential is systematically varied during analysis

Potentiometry

- Simply means measuring of electric potentials in electrochemical cells (galvanic cell)

- *Potentiometric Methods:* is a field of electro-analytical method based on measurements of the potential of electrochemical cells in the absence of appreciable currents ($I \rightarrow 0$)

- Potentiometric measurements are made using a potentiometer to determine the difference in potential between a **working (or indicator) electrode** and a **reference electrode**

$$E_{cell} = E_{indicator} - E_{reference}$$

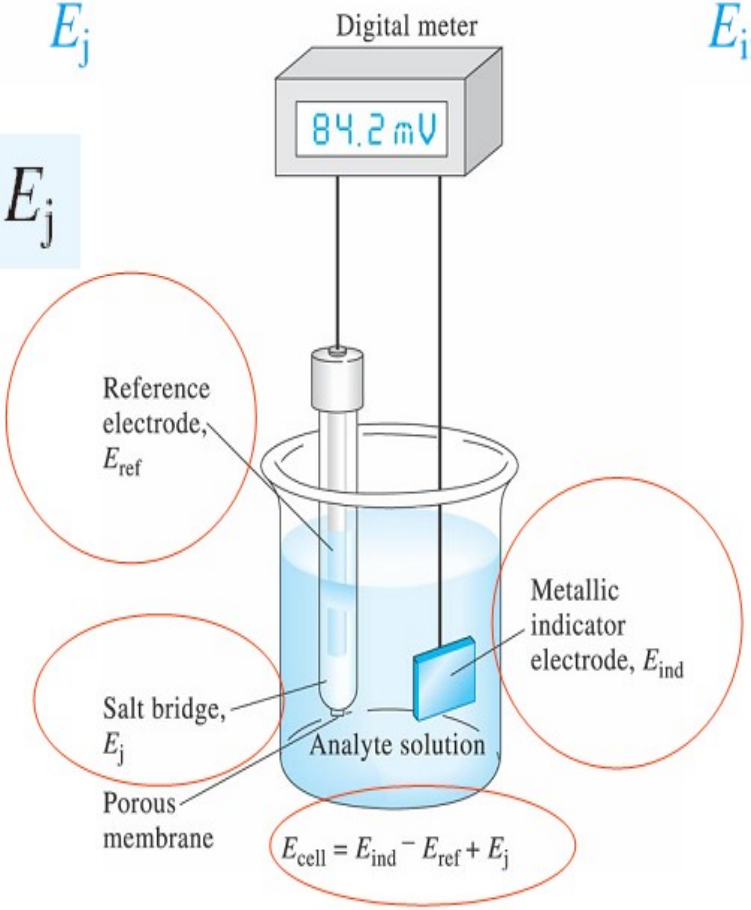
- **typical cell for potentiometric analysis:**

reference electrode | salt bridge | analyte solution | indicator electrode

E_{ref} E_j E_{ind}

$$E_{cell} = E_{ind} - E_{ref} + E_j$$

For most electroanalytical methods, the junction potential is small enough to be neglected.



- Reference electrode
  - A half-cell with an accurately known electrode potential,
  - independent of the concentration of the analyte or any other ions in the solution
  - Always treated as the left-hand electrode
- Indicator electrode
  - Which is immersed in a solution of the analyte, develops a potential,
  - depends on the activity of the analyte.
  - Is selective in its response
- Salt bridge
  - Preventing components of the analyte solution from mixing with those of the reference electrode
  - A potential develops across the liquid junctions at each end of the salt bridge.
  - Potassium chloride is a nearly ideal electrolyte for the salt bridge because the mobilities of the K^+ ion and the Cl^- ion are nearly equal.

- Nernst equation is the basis for the relationship between the voltage generated by an electrochemical cells as a result of the two half cell reactions and the relevant concentration at each electrode.

- The potential difference between the two electrodes therefore depends upon **composition of the solution** and the **reversibility of the redox couples of the species** present in the solution.

- Nernst equation for a redox electrode may be given as
  - ✓ $E = E^{\circ}_{ox,red} + (RT/nF).\ln (a_{ox}/a_{red})$
  - ✓ $E = E^{\circ}_{ox,red} + (0.0592/n).\log_{10} (a_{ox}/a_{red})$

Potentiometry

Electrode potential developed between:

Indicator electrode

- **Potential** (E_{ind}) varies
- **Depends on** the analyte **concentration**

Reference electrode

- Known, **constant potential** (E_{ref})
- **Independent of the** analyte **concentration**

Common reference electrodes:

Solid metal / its ''unsoluble" salt / saturated conc. of anion

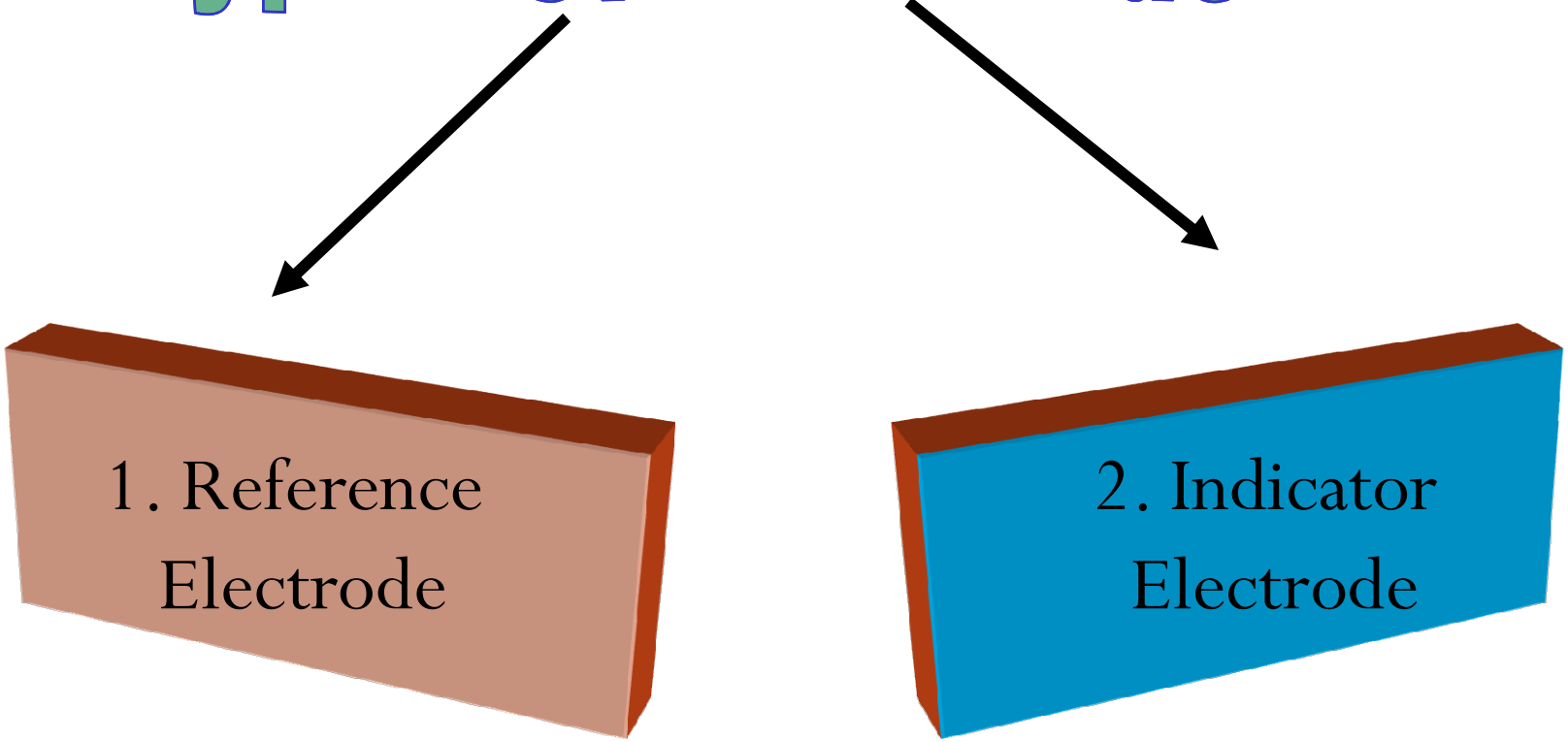
e.g. Ag / AgCl / KCl
Hg / Hg_2Cl_2 / KCl
Hg / Hg_2SO_4 / K_2SO_4
Pt(*s*), H_2 (*g*, 1 atm) | H^+

$$E = E_0 + \frac{0.059}{n} \log c$$

Nernst equation:

Glass electrode	**Neutralization titration:**	$E = E_0 + 0.059 \log [H^+]$
Metal electrode	**Complexometric titration:**	$E = E_0 + \frac{0.059}{n} \log [M^{n+}]$
Ion-selective electrode	**Precipitation titration:**	$E = E_0 + 0.059 \log [X^-]$
Nobel metal electrode	**Redox titration:**	$E = E_0 + \frac{0.059}{n} \log \frac{[ox]}{[red]}$

Types Of Electrodes



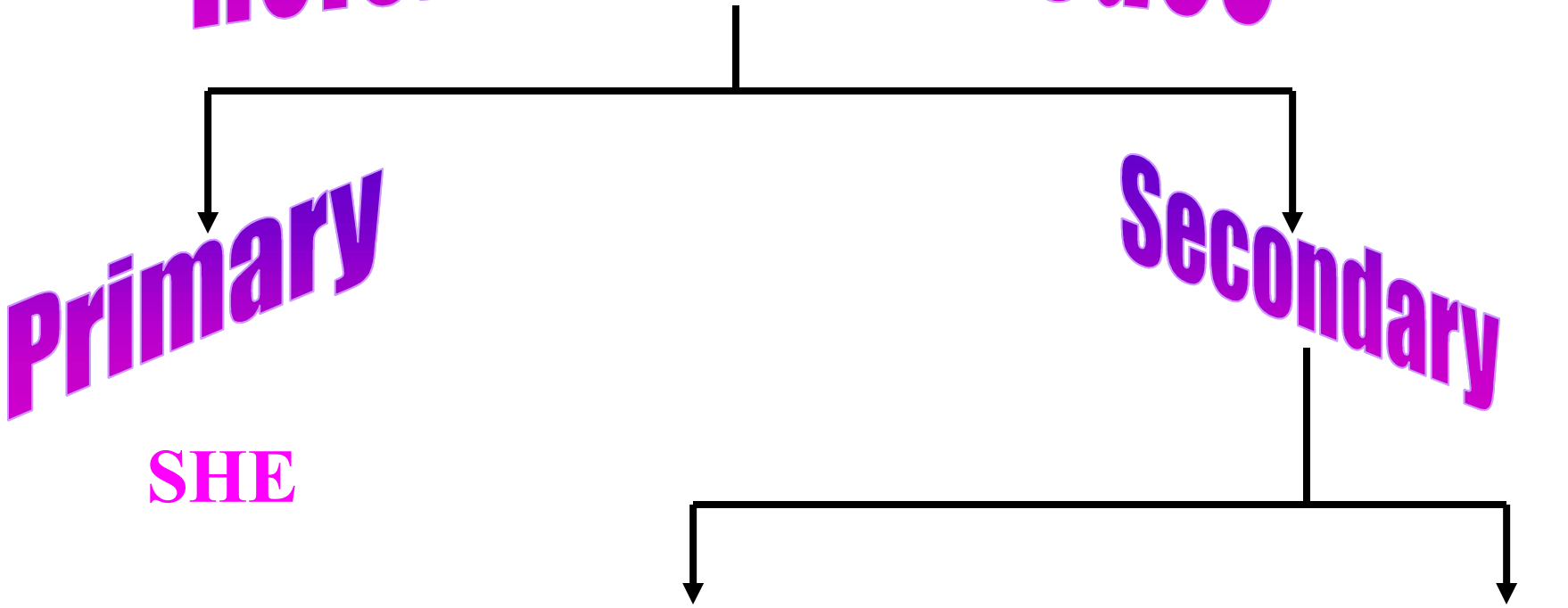
1. Reference electrodes

- Is a half-cell having **a known electrode potential** that remains **constant** and is **independent** of the composition of the analyte solution

- Used for half of the cell to determine the potential of the analyte of interest

- The ideal reference electrode must provide a stable potential.
  - so that any change in E_{cell} is attributed to the indicator electrode, and, therefore, to a change in the analyte's concentration
- In addition, the ideal reference electrode should be **easy to make and to use**

Reference Electrodes



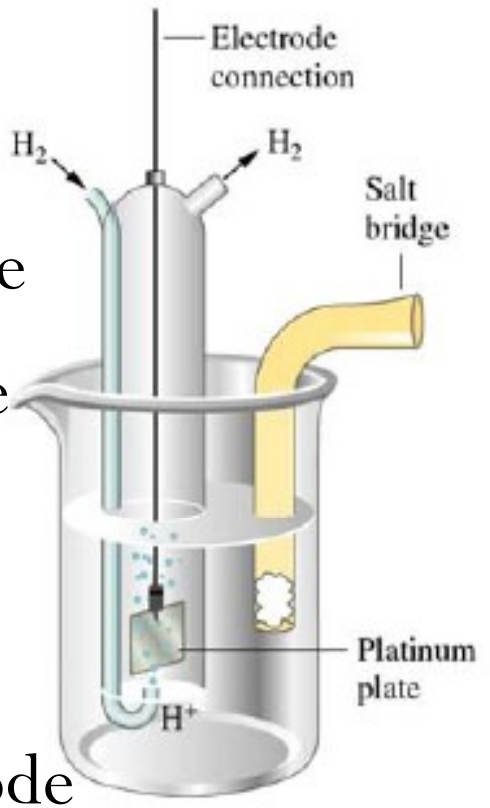
- The commonly used reference electrodes are:
  - Normal or Standard Hydrogen electrode (SHE)
  - Saturated calomel (Hg_2Cl_2) electrode (SCE)
  - Silver-Silver chloride (Ag/AgCl) electrode

- the later two are more frequently used because they have a **more practical construction**

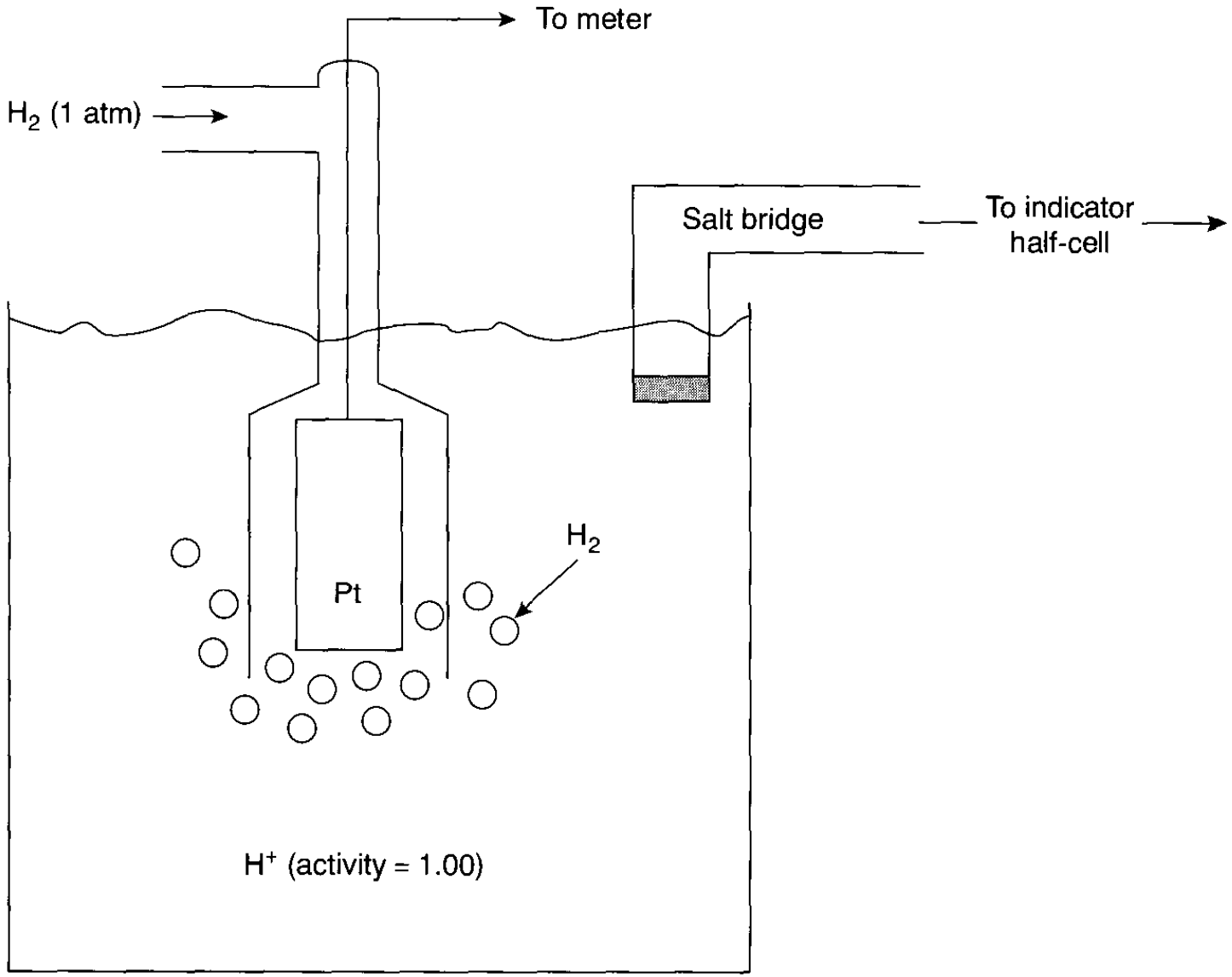
1.1. Standard Hydrogen electrode (SHE):

- It is the primary reference electrode
  - All electrode potentials are quoted with reference to it
- It consists of a piece of platinum foil coated with platinum black
  - has the property of adsorbing large quantities of atomic hydrogen and
  - it permits the change from the gaseous to the ionic form and the reverse process to occur without hindrance;

- which is immersed in a solution of hydrochloric acid containing hydrogen ions at unit activity (**1.18 M** HCl at 25^0 C)
- Hydrogen gas in a pressure of one atmosphere is passed over the platinum foil through a side tube and escapes through small holes in the glass tube.
- Under these conditions, the hydrogen electrode has a definite potential equal to **zero** at all temperatures



Standard hydrogen electrode



Schematic diagram of the standard hydrogen electrode (SHE)

- Despite its importance as the fundamental reference electrode against which all other potentials are measured, the SHE is **rarely** used because it is **difficult to prepare and inconvenient to use**
- The shorthand notation for the standard hydrogen electrode is: $Pt(s), H_2(g, 1\ atm) \mid H^+ (a = 1.00) \mid\mid$
- Reduction half reaction:

$$2H^+(aq) + e^- \rightleftharpoons H_2(g)$$

- SHE.mp4

Limitation

- It is difficult to be used and to keep H_2- gas at one atmosphere during all determinations
- It needs **periodical replacing** of Pt Sheet with Pt Black

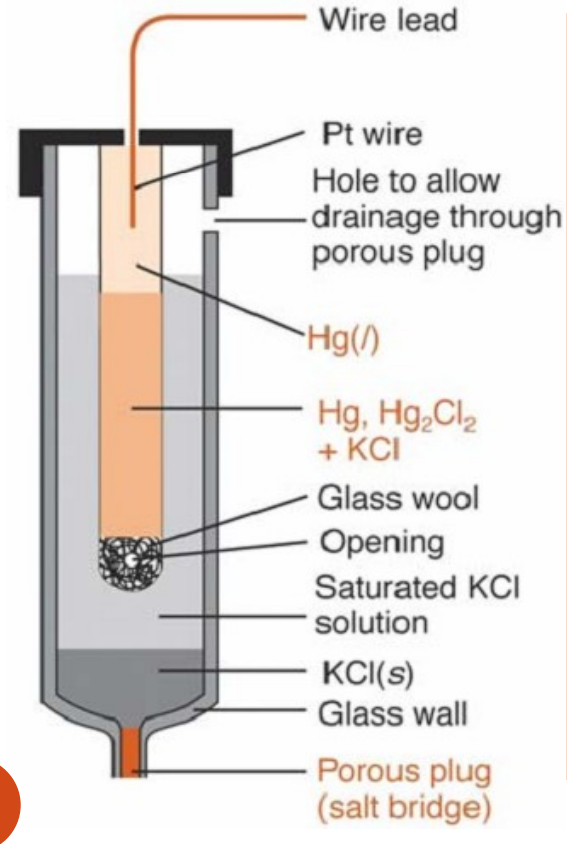
1.2. Calomel Electrode (Hg in contact with Hg_2Cl_2 & KCl)

- Saturated Calomel Electrode (SCE) very widely used

  Half Cell: Hg/Hg_2Cl_2 (satd), KCl (xM) | |

  Half Reaction: $Hg_2Cl_2 (s) + 2e^- \leftrightarrow 2Hg + 2Cl^-$

  - Note: response is dependent on [Cl-]



Calomel Electrode

- It contains of an inner jacket and outer sleeve
- Inner jacket has wire contact with Hg and plugged with a mixture of calomel Hg2Cl2 & KCl
- Outer sleeve – crystals of KCl & porous plug of asbestos
- Space between inner jacket & outer sleeve is usually filled with saturated KCl
- Merits of SCE
  - Ease of construction
  - Stability of potential

- The SCE has the advantage that the concentration of Cl^-, and, therefore, the potential of the electrode, remains constant even if the KCl solution partially evaporates

- A significant disadvantage of the SCE is that the solubility of KCl is sensitive to a change in temperature

  ➢ At higher temperatures the concentration of Cl^- increases, and the electrode's potential decreases

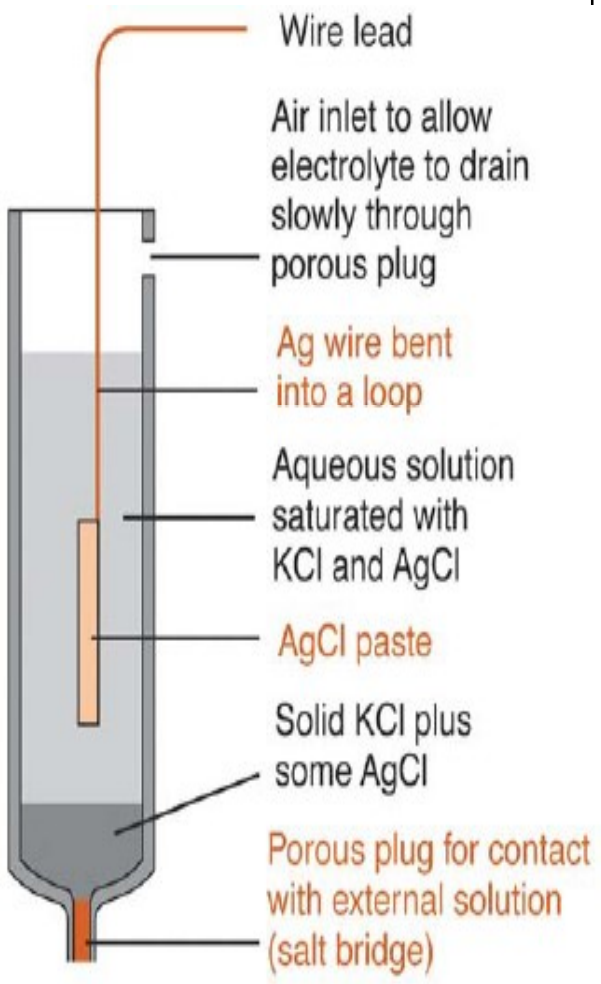
1.3. Silver/Silver Chloride Electrode

- Most widely used reference electrode system
- Ag electrode in KCl solution saturated with AgCl

Half Cell: Ag/AgCl (satd), KCl (xM) | |

Half Reaction: $AgCl(s) + e^- \leftrightarrow Ag(s) + Cl^-$

- **Advantage:** one advantage over SCE is that Ag/AgCl electrode can be used at temperatures > 60°C
- **Disadvantage:** Ag reacts with more ions


Wire lead
Air inlet to allow electrolyte to drain slowly through porous plug
Ag wire bent into a loop
Aqueous solution saturated with KCl and AgCl
AgCl paste
Solid KCl plus some AgCl
Porous plug for contact with external solution (salt bridge)

2. Indicator electrode

- They are electrodes used with reference electrode to measure **potential of unknown solution**
- The potential of the indicator electrode in a potentiometric electrochemical cell is **proportional to the concentration of analyte**
- They are either **specific** (for one ion) or **selective** (for several ions)

- **Two general** types are known:

1. **Metallic** and
   - where the **redox reaction** takes place at the **electrode surface**
2. **Membrane (ion-selective) electrodes**
   - where **charge exchange takes** place at a **specific surfaces** and as a result a **potential is developed**

1. Metallic Indicator Electrode

- **Different kinds of metallic indicator electrodes:**
  - ❖ Metallic Electrodes of the First Kind
    - ➢ Involves single reaction
    - ➢ Metal rod immersed in its solution
    - ➢ Example: use of copper electrode to detect Cu^{2+} in solution

½ reaction: $Cu^{2+} + 2e^- \leftrightarrow Cu\ (s)$

E_{ind} gives direct measure of Cu^{2+}:

$$E_{ind} = E^o_{Cu} - (0.0592/2) \log [Cu]/[Cu^{2+}]$$

since $a_{Cu(s)} = 1$:

$$E_{ind} = E^o_{Cu} - (0.0592/2) \log 1/[Cu^{2+}]$$

- **Limitations:**
  - not very selective
  - **many can only be used at neutral pH →metals dissolve in acids**
  - some metals readily oxidize
  - certain hard metals (Fe, Cr, Co, Ni) do not yield reproducible results

❖ Metallic Electrodes of the Second Kind

- Detection of **anion derived** from the interaction with metal ion (M^{n+}) from the electrode
- Anion forms precipitate or stable complex with metal ion (M^{n+})
- Example: Detection of Cl^- with Ag electrode

½ reaction: $AgCl(s) + e^- \leftrightarrow Ag(s) + Cl^-$ $\quad E^O = 0.222\,V$

E_{ind} gives direct measure of Cl^-:

$$E_{ind} = E^o - (0.0592/1) \log [Ag]\,[Cl^-]/[AgCl]$$

since $a_{Ag(s)}$ and $a_{AgCl(s)} = 1$ & $E^o = 0.222\,V$:

$$E_{ind} = 0.222 - (0.0592/1) \log [Cl^-]$$

❖ Metallic Redox Indicators

- Electrodes made from inert metals (Pt, Au, Pd)
- Used to detect oxidation/reduction in solution
- Electrode acts as e- source/sink
- Example: Detection of Ce^{3+} with Pt electrode

½ reaction: $Ce^{4+} + e^- \leftrightarrow Ce^{3+}$

E_{ind} responds to Ce^{4+}:

$$E_{ind} = E^o - (0.0592/1) \log [Ce^{3+}]/[Ce^{4+}]$$

- Problems:
  - Electron-transfer processes at inert electrodes are frequently not reversible

2. Membrane Indicator Electrodes (Incorporate in your assignment)